A method for preparing a vinyl polymer-polyolefine composite.

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Description

The invention relates to a method for preparing a vinyl polymer - polyolefine composite.

The present invention relates to a new way of preparing a polyolefine composite, which can be applied to be used as such and worked into various articles, e.g. as foam plastic or as a component in semiconducting layers on electric cables. The composite is comprised of a polyolefine and a vinyl polymer, and the invention relates to the preparation of this composite by polymerizing the vinyl monomer inside the polyolefine particles.

For improving rigidity, dimensional stability, printability and the like of polyolefines, which are to be worked into various articles or which are to be foamed into foam plastic, attempts have been made to blend the polyolefine with some vinyl polymer, e.g. polystyrene. Due to the low compatibility of polystyrene in polyolefines, it has proved to be difficult to obtain homogenous blends with an attractive appearance. Already on small amounts, 0.2-10% by weight, the blend gets a low impact resistance and an impaired appearance.

For avoiding these problems, attempts have been made to polymerize styrene inside the polyolefine particles. Basically two different methods of polymerizing styrene in situ in the polyolefine particles have been suggested, and both methods are based on the fact that styrene is allowed to diffuse into the polyolefine particles, after which the polymerization of styrene occurs in a basically traditional way. The greatest difference between the two methods is the way, in which styrene is allowed to diffuse into the polyolefine particles.

In the West German patent DE 29 07 662 is described the polymerization of styrene in situ in several different polyolefines. In this method, styrene is added slowly into a water suspension containing polyolefine particles at an elevated temperature. This means that impregnation and polymerization of the styrene occur simultaneously with the result that the polymerization tends to occur more in the surface regions of the polyolefine particles, which results in that the polystyrene is concentrated on the surface layer of the polyolefine particles.

In the US patent 4.412.938 is described the polymerization of styrene in situ in an ethylene vinyl acetate copolymer. In this method, all styrene is added at a time into a water suspension containing ethylene vinyl acetate copolymer particles. The styrene is added at so low a temperature that no polymerization occurs. Only after all styrene or most of the styrene has diffused into the ethylene vinyl acetate copolymer particles, the temperature is increased and the polymerization starts. A disadvantage of this method is that it lasts several hours before the styrene has diffused into the ethylene vinyl acetate copolymer particles. The method is in other words time-consuming.

In this patent is described the preparation of a polyolefine - vinyl polymer composite by means of a method, which avoids the problems and disadvantages related to above-mentioned preparation methods. However, the method maintains the good sides of the above-mentioned methods, which good sides are that a homogenous blend of the polyolefine and the vinyl polymer is obtained and that the polymerization product is obtained in a particle form.

The inventive method is mainly characterized in that

a) 10-200 weight fractions of vinyl monomer and 0.01-4.0 weight fractions, based on 100 weight fractions of vinyl monomer, of a free radical polymerization Initiator is impregnated in 100 weight fractions of polyolefine particles by slowly blending these at a temperature of 20-100 °C while continuously or discontinuously adding 1-60% by weight of water, based on the total weight of the vinyl monomer and the polyolefine, during the maintenance of the particle structure of the polyolefine;

b) a water suspension is prepared by adding to the above-mentioned blend after a completed impregnation suspension water, whereby the total quantity of water becomes 80-1000 weight fractions, based on 100 weight fractions of polyeolone + vinyl monomer, as well as a stabilizing agent;

c) the temperature of the water suspension is increased for polymerizing the vinyl monomer.

The preferred embodiments of the invention are given in the subclaims.

After the 100 weight fractions of polyolefine particles have been blended with 10-200 weight fractions of vinyl monomer and 0.01-4 weight fractions, based on 100 weight fractions of monomer, of a free radical initiator, the blend is agitated slowly at so low a temperature that no decomposition of the initiator and no polymerization occur, but the temperature is yet so high that the polyolefine particles are impregnated with the monomer. During this impregnation phase, a small part of water is added at the same rate as the vinyl monomer impregnates the polyolefine. Alternatively, a small part of water can be added as a batch at the start of the impregnation. When all monomer and Initiator or most of them has diffused into the polyolefine particles, the suspension water and a stabilizing agent are added. After this, the temperature is increased and the polymerization starts. After completed polymerization, the polymerization product is washed and dried.
In this method for preparing a polyolefine-vinyl polymer composite, the absorption of the styrene first occurs in the absence of water and thereafter in the presence of only a small amount of water. This means that the monomer, to be able to penetrate into the polyolefine particles, has to be transported through only a small amount of water, which means that the impregnation is more rapid than in the method described in the US patent 4,412,938. During the impregnation, the polyolefine particles partly swell depending on how much vinyl monomer has been added, but the particle form of the polyolefine is still maintained.

In Neste Oy's patent application 894461 is described a method for preparing a polyolefine-vinyl polymer composite, in which method the impregnation occurs totally in the absence of water. In comparison with the application 894461, the present method has two advantages. Firstly, the power demand of the agitator motor is lower, since the water present during the impregnation has a "lubricating" effect on the mixing of the polyolefine particles. Secondly, there is no risk that the particles break down, since the space between the particles is at the start filled with the monomer, later with the monomer and water and finally at least partly with water.

The invention is next described in detail.

**Polyolefine**

Useful polyolefines include high density polyethylene, low density polyethylene and linear low density polyethylene. The polyethylene can be a homopolymer or a copolymer. The comonomer can be e.g. vinyl acetate, acrylic acid, methacrylic acid, methylacrylate, methyl methacrylate, ethyl acrylat and ethylmethylacrylate, butyl acrylate and butylmetacrylate, vinyl chloride, propene or other α-olefin. Ethylene-α-olefine-polymeretylpolymers can also be used. Useful α-olefines include propene, butene, pentene, isoprene, hexene or their mixtures, and useful polyenes include hexadiene-1,4, hexadiene-1,5, heptadiene-1,6, 2-methyl pentadiene-1,4, octadiene-1,7, 6-methyl heptadiene-1,5, octatriene, dicyclo pentadiene. In case the ethylene polymer is a copolymer, the share of the ethylene in the copolymer must be at least 50% by weight.

The polyolefine can also be comprised of propene and its copolymer. The propene polymers can consist of more than 50% by weight of propene and the comonomer can be ethylene or some α-olefin or some polar unsaturated monomer.

Poly(ethylene-co-vinylacetate) has proved to be especially suitable as a polyolefine in the preparation of polyolefine vinyl polymer composites. In this case, the share of the vinyl acetate in the copolymer must be 1-35% by weight.

The polyolefine must be in a particle form with a particle size of 0.5-10 mm, most preferably 1-6 mm. When the polyolefine is in a particle form, it is easy to achieve a good agitation during the impregnation phase, which is a precondition for the fact that the concentration of the vinyl monomer becomes the same in all polyolefine particles. If the particles are too large, it may be difficult to keep the suspension stable during the final step of the polymerization. Stability problems can also occur in connection with small particles.

**Vinyl monomer**

Useful vinyl monomers are e.g. aromatic vinyl monomers of the type styrene and substituted styrenes. Substituted styrenes can have the substituent on the benzene ring, such as in methyl styrene, isopropyl styrene or on the α-carbon, such as in α-methyl styrene and α-ethyl styrene. The above-mentioned or their mixtures can be used as a vinyl monomer. Comonomers for the above-mentioned aromatic vinyl monomers can be used together with other vinyl monomers, e.g. acrylonitrile, C1-C7 alkyl acrylates, C1-C7-alkyl methacrylates, vinyl halides, metacrylonitrile, maleic anhydride, acryl amide and metacryl amide. The amount of this other vinylmonomer is up to 50% by weight of the total amount of vinyl monomer. Styrene has proved to be especially suitable for the preparation of polyolefine-vinyl polymer composites.

**Quantity of vinyl monomer**

The quantity of the vinyl monomer to be polymerized in the polyolefine matrix is 10-200 weight fractions, based on 100 weight fractions of polyolefine. A larger quantity of vinyl monomer than 200 weight fractions causes problems such that it is difficult to keep the polyolefine in a particle form during the impregnation; the particles tend to agglomerate and form a homogenous phase. It is not appropriate to add a smaller quantity of vinyl monomer than 10 weight fractions, since such quantities of vinyl monomer provide only small changes in the properties of the initial polyolefine.

**Initiator**

Initiators, which are used for polymering the vinyl monomer, are initiators, which are conventionally used in the suspension polymerization and include organic peroxides, such as benzoyl peroxide, lauroyl peroxide, t-butyl perbenzoate, t-butyl-peroxy-2-ethyl hexanate, t-butyl peroxides, dicumyl peroxyde, di-t-butyl peroxide, bis(t-butyl peroxy-
Impregnation of vinyl monomer

Accordingly, the invention is characterized by the fact that during the impregnation of the vinyl monomer in the polyolefine particles, part of the water is added continuously or discontinuously in small batches. The purpose of this water is to fill the empty space forming between the particles, when the vinyl monomer is absorbed in the polyolefine particles. This water thus decreases the friction between the particles and thereby prevents the particles from breaking down. Due to the decreased friction, also the power demand of the agitator motor is lower.

Another embodiment of this invention is that the amount of water to be added during the impregnation is lower than what is needed for filling the empty space between the polyolefine particles. This water can be added all at a time at the start of the impregnation or continuously during the impregnation process. Also in this case, the water decreases the friction between the particles and thereby decreases the risk that the particles break down, and the power demand of the agitator motor becomes lower. The impregnation is done in such a way that polyolefine particles, styrene and initiators are batched into a reactor in any order. If the initiator or the initiators are in a powder form, they are preferably dissolved in part of or in the total amount of vinyl monomer for ensuring that the concentration of the initiator becomes the same in the different polyolefine particles.

The impregnation is thus started in the absence of water, but the addition of water is started immediately when the polyolefine particles begin to absorb by the vinyl monomer. The maximum amount of water to be added during the impregnation, i.e. the amount of water which is needed to be able, at the end of the impregnation when all vinyl monomer is absorbed by polyolefine particles, to totally fill the empty space between the particles, is of the order 60% by weight of the total amount of polyolefine and vinyl monomer. Of the total amount of water present in the suspension phase the maximum amount of water added during the impregnation covers 6-75%, and more preferably 15-60%.

The minimum amount of water to be added during the impregnation is the amount of water, which is needed to decrease the friction between the particles, and this amount of water is > 1.0% by weight of the total amount of polyolefine and vinyl monomer.

The temperature during the impregnation is 20-100 °C depending on the type of polyolefine and vinyl monomer, i.e. depending on how easily the vinyl monomer penetrates into the polyolefine. The impregnation temperature is to be so low that practically no polymerization occurs during the impregnation phase. The impregnation temperature must thus be observed when selecting the initiator.

For keeping the concentration of the vinyl monomer the same in the different polyolefine particles, the contents of the reactor must be slowly bed during the impregnation. The agitation rate expressed as the top speed of the agitator is not critical, but it is preferably in the range 0.1-1.0 m/s. If the agitation rate is too low, the vinyl monomer can be unevenly distributed between the polyolefine particles.

The impregnation can be ceased when all or practically all vinyl monomer has diffused into the polyolefine particles. This is in practice controlled simply by taking a sample of the liquid in the reactor. The sample soon separates into a water phase and a vinyl monomer phase. When the amount of the non-absorbed vinyl monomer, which thus corresponds to the amount of vinyl monomer in the sample, is smaller than 10% by weight of the total amount of the vinyl monomer phase in the sample, the suspension step can be started. The remaining free vinyl monomer is absorbed by the polyolefine particles at the start of the suspension step.

The impregnation generally lasts for 0.2-3.0 hours depending on how easily the vinyl monomer penetrates into the polyolefine particles and depending on whether the impregnation has been performed at an elevated temperature or not. It is not necessary to perform the impregnation in the same reactor as the polymerization.

Preparation of water suspension

After the impregnation has been completed, the suspension water and the suspending agents are added, and the agitation rate is increased to values normal in connection with suspension polymerization, i.e. to such values that it is possible to maintain a good agitation in the reactor and keep the suspension stable.

Such substances can be used as suspending agents, which are normally used in suspension polymerization of vinyl monomers. These include e.g. water soluble polymers, such as polyvinyl al-
cohol, polyvinyl pyrrolidone and methyl cellulose or partially water soluble substances, such as calcium triplosphate and magnesium pyrophosphate.

The total amount of water, i.e. the amount of water to be added during the impregnation plus the amount of water added for preparing the water suspension, is not critical, but it must be so large that the suspension is maintained during the polymerization, which equals 80-1000 weight fractions, more preferably 100-500 weight fractions of water on 100 weight fractions of polyolefine + vinyl monomer.

If the impregnation has been performed at an elevated temperature, the water is preferably heated to the same temperature, before it is blended with the polyolefine particles swollen by the vinyl monomer. This prevents the vinyl monomer from diffusing out of the polyolefine particles due to the sudden decrease in temperature in case the temperature of the water added is lower than the temperature of the polyolefine impregnated with the vinyl monomer.

**Polymerization of vinyl monomer**

The polymerization of the vinyl monomer which has absorbed into the polyolefine particles occurs by raising the temperature in the agitated reactor, whereby the initiator decomposes and initiates the polymerization. The polymerization can be performed at one or more temperatures within the temperature range 50-140 °C. The polymerization can preferably be started at a low temperature 50-90 °C and thereafter completed at a high temperature 90-140 °C. The whole polymerization generally lasts for 5-20 hours.

After the polymerization has been completed, the reactor is cooled and the product is then finished in a way normal in the suspension polymerization (e.g. washing and drying), and it is then ready for further treatment.

The polyolefine particles retain their particle form during the polymerization. In comparison with the original polyolefine particles, the particles are after the polymerization only slightly larger depending on the absorbed and polymerized vinyl monomer.

**Properties of polymerization product**

The polymerization product provides a homogenous impression and is esthetically attractive. The vinyl polymer polymerized in the polyolefine particle is distributed on particles of a size 0.05-2.0 μm, which are homogenously distributed in the polyolefine matrix. The concentration of the vinyl monomer is as high in the middle as in the outer regions of the particle, determined from infrared microscopy.

Since the vinyl monomer is polymerized inside the polyolefine particle, part of the polymerized vinyl monomer is in the form of a homopolymer and part in a form grafted on the polyolefine. Even though the share of the grafted vinyl polymer is considerably smaller than the share of the homopolymer, its existence is important for the morphological stability of the composite during processing.

A feature of this invention is that the morphology of the composite remains unchanged after treatment, i.e. that the vinyl polymer remains in the form of a pearl with a size of 0.05-2.0 μm homogenously distributed in the polyolefine matrix. The processing of the composite is simple depending on the wide temperature range for processing as well as on the suitable melt index at the processing temperature.

In comparison with unmodified polyolefines, the composites prepared according to this patent have improved mechanical properties, such as hardness, rigidity and in certain cases strength.

**Usage of composite**

Polymer composites prepared according to this patent can be used in many different ways mainly depending on the type of polyolefine and vinyl monomer used as well as their mutual proportions.

Accordingly, it is e.g. possible to increase the mechanical strength on many polyolefines by polymerizing in situ a vinyl monomer inside the polyolefine. Also e.g. the hardness and rigidity on the ethylene vinyl acetate copolymer and polypropene can be increased by polymerizing into these in situ styrene. These composites can be used as such and worked into various articles. The composites can also be blended with other thermoplasts, whereby the resultant composite has above-mentioned advantages.

Ethylene vinyl acetate copolymer - polystyrene composites can be impregnated with some conventional volatile media, such as iso- or n-pentane, and thereafter expanded with water vapour into foam plastic. Such a foam plastic has better elastic properties and a better resistance to chemicals than polystyrene foam.

Polypropene-polystyrene composite films prepared according to this invention can be stretched in one or two directions and then used as synthetic paper.

Ethylene vinyl acetate copolymer - polystyrene composites can be one component in the semiconductor layer of electric cables, which are thereby easy to strip from the cable during coupling work.
EXAMPLES

Example 1

50 weight fractions (1000 g) of ethylene vinyl acetate copolymer particles with a diameter of 3-4 mm were added into a 1-liter reactor. The ethylene vinyl acetate copolymer (EVA) was Neste Oy’s commercial product EVACO B 5028 and contains 28% by weight of vinyl acetate and its melt index was 5 g/10 min, measured according to the standard ISO 1133, 2.16 kg and 190 °C. 50 weight fractions of styrene and as initiators 0.15 weight fractions of azobis-isobutyl nitrile, 0.1 weight fractions of benzoyl peroxide and 0.075 weight fractions of t-butyl peroxybenzoate were added thereafter. The blend was agitated slowly, 2-20 revolutions per minute, at room temperature. After an impregnation of 10 minutes, water was added in small doses of 3.35 weight fractions at intervals of 2-4 minutes. Altogether 60 weight fractions of water was added during 50 minutes. The maximum torque of the agitator was 70 Ncm.

After this, the water suspension was prepared by further adding 290 weight fractions of water and as stabilizing agents 1.0 weight fractions of tricalcium phosphate and 0.03 weight fractions of sodium dodecyl benzene sulphonate. The agitation rate was then increased to 200 revolutions per minute.

The polymerization was started by raising the temperature to 55 °C and by keeping it there for three hours. The temperature was then raised to 90 °C during 8 hours. After one hour at 90 °C the temperature was raised to 120 °C during 1.5 hours and maintained there for 3 hours.

After cooling the reactor was emptied and the 4-5 mm EVA-poly styrene composite particles were washed and dried. The particles were white and homogenous. It could be observed by means of a scanning electron microscope that the polystyrene was dispersed as round pearls of ca. 0.1-0.5 μm in the EVA matrix.

Comparison example

This experiment was performed according to the experiment 1 with the difference that no water was added during the impregnation phase. In this case, the maximum torque of the agitator was 120 Ncm.

Example 2

50 weight fractions (300 g) of EVACO B 5028 with a diameter of 3-4 mm were added to a 3-liter reactor. After this, 50 weight fractions of styrene and as initiators 1.5 weight fractions of di-cetyl peroxydicarbonate and 0.05 weight fractions of benzoyl peroxide were added. The blend was agitated slowly, 20-30 revolutions per minute, at 25 °C. After an impregnation of 10 minutes, 8 weight fractions of water were added and the impregnation was continued for 35 minutes.

The water suspension was then prepared by adding 280 weight fractions of water, 1 weight fraction of tricalcium phosphate and 0.03 weight fractions of sodium dodecyl benzene sulphonate. The agitation rate was then raised to 240 revolutions per minute.

The polymerization was started by raising the temperature to 53 °C and therefrom to 65 °C during 8 hours. After one hour at this temperature the temperature was raised to 90 °C during 2 hours and maintained there for 2 hours. The polymerization product was finished in the same way as in Example 1 and it proved to have the same structure and appearance as in Example 1.

Claims

1. A method for preparing a polyolefine-vinyl polymer composite, characterised in that
   a) 10-200 weight fractions of vinyl monomer and 0.01-4.0 weight fractions, based on 100 weight fractions of vinyl monomer, of a free radical polymerisation initiator are impregnated into 100 weight fractions of polyolefine particles by blending these at a temperature of 20-100 °C, while continuously or discontinuously adding 1-60% by weight of water based on the total weight of the vinyl monomer and the polyolefine, during the maintenance of the particle structure of the polyolefine;
   b) a water suspension is prepared by adding to the above-mentioned mixture after a completed impregnation suspension water, whereby the total quantity of water becomes 80-1000 weight fractions, based on 100 weight fractions of polyolefine and vinyl monomer, as well as a stabilising agent;
   c) the temperature of the water suspension is increased to polymerise the vinyl monomer.

2. A method according to Claim 1, characterised in that the polyolefine is a polyethylene or an ethylene copolymer containing more than 50% by weight of ethylene, in which the comonomer can be, e.g. vinyl acetate, an α-olefine, acrylic or methacrylic acid or an ester thereof or polyene or vinyl chloride.
3. A method according to Claim 1, characterised in that the polyolefine is a polypropylene or a propylene copolymer containing more than 50% by weight of propylene, in which the comonomer can be, e.g. ethylene, an α-olefine or another polar unsaturated monomer.

4. A method according to any one of the preceding Claims, characterised in that the diameter of the polyolefine particles is 0.5-10 mm.

5. A method according to any one of Claims 1-4, characterised in that the vinyl monomer is an aromatic vinyl monomer or a substituted styrene, such as methyl styrene of α-methyl styrene.

6. A method according to any of Claims 1-5, characterised in that up to 50% by weight of the aromatic vinyl monomer can be replaced by another monomer, which may be, e.g. acrylonitrile, methacyronitrile, a C₁-C₇ alkylic acrylate or C₁-C₇ alkyl methacrylate, a vinyl halides, maleic acid anhydride, acrylamide or methacrylamide.

7. A method according to any of the preceding Claims, characterised in that the initiator is an organic free radical polymerisation initiator, such as a peroxide or an azo compound, e.g. benzoyl peroxide, lauroyl peroxide, t-butyl peroxoxybenzoate, dicumyl peroxide or azobisisobutyronitrile.

8. A method according to any of the preceding Claims, characterised in that the polymerisation of the vinyl monomer is effected at a temperature of 50-140 °C.

9. A method according to any of the preceding Claims, characterised in that the vinyl monomer is polymerised inside the polyolefine particles, so that the vinyl polymer is homogenously dispersed as round pearls, with a size of 0.05-2.0 μm, in the polyolefine matrix.

Patentansprüche

1. Verfahren zum Herstellen eines Polyolefin-Vinyldopolymer-Verbundstoffes, dadurch gekennzeichnet, daß
(a) 10 bis 200 Gewichtsteile Vinylmonomer und 0,01 bis 4,0 Gewichtsteile eines radikalen Polymerisationsinitiators bezogen auf 100 Gewichtsteile Vinylmonomer dadurch in 100 Gewichtsteilen Polyolefinpartikeln imprägniert werden, daß diese bei einer Temperatur von 20° bis 100° C kompoundiert werden, während kontinuierlich oder diskontinuierlich 1 bis 60 Gewichtsprozent Wasser bezogen auf die Gesamtmasse des Vinylmonomers und des Polyolefins unter Bewahrung der Partikelstruktur des Polyolefins zugesetzt werden;
(b) eine wässrige Suspension hergestellt wird, indem zu der vorgenannten Mischung nach beenderter Imprägnierung Suspendierwasser zugesetzt wird, wodurch die Gesamtmenge Wasser bezogen auf 100 Gewichtsteile Polyolefin und Vinylmonomer auf 80 bis 1.000 Gewichtsteile wächst; sowie ein Stabilisiermittel zugesetzt wird;
(c) die Temperatur der wässrigen Suspension erhöht wird, um das Vinylmonomer zu polymerisieren.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Polyolefin ein Polyethylen oder ein Ethylen-Copolymer ist, enthaltend mehr als 50 Gewichtsprozent Ethylen, wobei das Comonomer beispielsweise sein kann: Vinylecetat, ein α-Olefine, Acryl- oder Methacrylsäure oder ein Ester davon oder Polyen oder Vinylchlorid.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Polyolefin ein Polypropylen oder ein Propylen-Copolymer ist, enthaltend mehr als 50 Gewichtsprozent Propylen, bei welchem das Comonomer beispielsweise sein kann: Ethylen, ein α-Olefine oder ein anderes polares ungesättigtes Monomer.

4. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Durchmesser der Polyolefinpartikel 0,5 bis 10 mm beträgt.

5. Verfahren nach Anspruch 1 bis 4, dadurch gekennzeichnet, daß das Vinylemonomer ein aromatisches Vinylemonomer vom Typ Styrol oder substituiertes Styrol ist, wie beispielsweise Methylstyrol oder α-Methylstyrol.


7. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der In-
iliator ein organischer, radikalischer Polymerisationsinitiator ist, wie beispielsweise ein Peroxid oder eine Azo-Verbindung, z.B. Benzoylperoxid, Laurylperoxid, t-Butylperoxybenzoat, Dichumylperoxid oder Azo-bis-isobutyronitril.


9. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Vinylmonomer im Inneren der Polylefinpartikel polymerisiert wird, so daß das Vinylpolymer in der Polylefin-Matrix homogen als runde Perlen mit einer Größe von 0,05 bis 2,0 μm dispergiert wird.

Rezrivendications

1. Procédé de préparation d’un produit composite de polymère vinyle et de polylefine, caractérisé en ce que
a) de 10 à 200 parties en poids d’un monomère vinyle et de 0,01 à 4,0 parties en poids, sur la base de 100 parties en poids de monomère vinyle, d’un initiateur de polymérisation par radicaux libres sont imprégnés dans 100 parties en poids de particules de polylefine en mélangeant ces dernières à une température comprise entre 20 et 100 °C tout en ajoutant d’une manière continue ou discontinue de 1 à 60% en poids d’eau sur la base du poids total du polymère vinyle et de la polylefine, pendant la conservation de la structure particulière de la polylefine;
b) on prépare une suspension aqueuse en ajoutant, au mélange susmentionné, après avoir obtenu une imprégnation complète, de l’eau de suspension, ce qui a pour résultat que la quantité totale d’eau atteint de 80 à 1000 parties en poids sur la base de 100 parties en poids de la polylefine et du monomère vinyle et on ajoute également un agent de stabilisation;
c) on élève la température de la suspension aqueuse pour polymériser le monomère vinyle.

2. Procédé selon la revendication 1, caractérisé en ce que la polylefine est un polyéthylène ou un copolymère d’éthylène contenant plus de 50% en poids d’éthylène, dans lequel le co-monomère peut être, par exemple, de l’acétate de vynile, une α-oléfine, de l’acide acrylique ou de méthacrylique ou un de leurs esters ou un polyène ou du chlorure de vynile.

3. Procédé selon la revendication 1, caractérisé en ce que la polylefine est un polypropylène ou un copolymère de propylène contenant plus de 50% en poids de propylène, dans lequel le co-monomère peut être, par exemple, de l’éthylène, une α-oléfine ou un autre monomère polaire non saturé.

4. Procédé selon l’une quelconque des revendications précédentes, caractérisé en ce que le diamètre des particules de polylefine est compris entre 0,5 et 10 mm.

5. Procédé selon l’une quelconque des revendications 1 à 4, caractérisé en ce que le monomère vinyle est un monomère vinyle aromatique du type styrène ou un styrène substitué comme un méthyl styrène ou l’α-méthyl styrène.

6. Procédé selon l’une quelconque des revendications 1 à 5, caractérisé en ce que jusqu'à 50% en poids du monomère vinyle aromatique peut être remplacé par un autre monomère qui peut être, par exemple, de l’acrylonitrile, du méthacrylonitrile, un acrylate d’alkyle en C₆- C₇ ou un méthacrylate d’alkyle en C₁₉- C₇, un halogène de vynile, de l’anhydride de l’acide maléique, de l’acrylamide ou de la méthacrylamide.

7. Procédé selon l’une quelconque des revendications précédentes, caractérisé en ce que l’initiateur est un initiateur de polymérisation par radicaux libres organique comme un peroxyde ou un composé azoïque, par exemple le peroxyde de benzoyle, du peroxyde de lauroyle, du peroxyde benzozate de t-butyly, du peroxyde de dicumyle ou de l’azobis-isobutyronitrile.

8. Procédé selon l’une quelconque des revendications précédentes, caractérisé en ce que la polymérisation du monomère vinyle est effectuée à une température comprise entre 50 et 140 °C.

9. Procédé selon l’une quelconque des revendications précédentes, caractérisé en ce que le monomère vinyle est polymérisé à l’intérieur des particules de polylefine de telle sorte que le polymère vinyle se trouve dispersé d’une manière homogène sous la forme de perles sphériques qui ont une taille comprise entre 0,05 et 2,0 μm dans la matrice de polye-